ligands. Since it appears to be advantageous to consider the solvated species as the entity undergoing reaction, this effect will be referred to as an *ion-structure* effect.

Effect of Solvent Composition on Rate of Dissociation.—The effect of solvent composition on the rate of dissociation presents a complicated situation. It is informative at this point to compare the dissociative behavior of the four complexes, $Fe(phen)_3^{2+}$, $Fe(bipy)_3^{2+}$, $Ni(phen)_3^{2+}$ and $Ni(bipy)_3^{2+}$, in methanol–water mixtures. This comparison is displayed graphically in Fig. 2. The relative rate constant is the ratio of the rate constant for a given complex in a given solvent mixture to the rate constant for the same complex in pure methanol. The logarithm of the relative rate constant has been plotted and, since the difference in the free energies of activation is proportional to this quantity, the ordinate has been marked in terms of both quantities. The rate constants for the iron(II) complexes are derived from the data of Table IV and hence are concerned with conditions where the salt effects have been kept as small as possible. The rate constants for the nickel(II) complexes are derived from the racemization data of Davies and Dwyer,[6] and it has been established[7] that the racemization rates are the same as the dissociation rates. These racemization measurements also were made under conditions where the salt effects were negligible.

At least three factors must be in operation here: one operating in the low methanol region tending to give decreasing rates, another in the intermediate region to give increasing rates, and the last to give decreases for high methanol content. An ion-structure effect, like that apparent from the racemization results, would be expected to favor increasing rates; this is probably the dominant factor in the intermediate region. The factor tending to give decreased rates in the low methanol region may be the disturbance of the solvent surrounding the ion caused by the necessary expansion of the dissociating species. Both the viscosity[6] and the volume shrinkage on mixing[19] suggest that the energy requirements of this *solvent-structure* effect would be greatest about mole fraction 0.3 methanol, if the solvent surrounding the ion had the same structure as the bulk solvent. Since the latter cannot be so, no exact correlation can be expected.

The remaining point to be explained is the decrease in rate in the high methanol content region. The simplest explanation is to correlate this with the deficiency of water in the solvated ion. If the dissociation mechanism includes participation by water, then the decrease is understandable. Some support for this view is to be found in the fact that the decrease in rate normally observed in high methanol content solutions is not evident when chloride is present (Table II). This could be accounted for by an internal ion-pair, in which the chloride ion is performing the function normally performed by a water molecule, *i.e.*, filling a vacated coördination site.

(19) C. Carr and J. A. Riddick, *Ind. Eng. Chem.*, **43**, 692 (1951).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

The Reaction of Bis-(cyclopentadienyl)-titanium(IV) Bromide with Different Chlorides in Various Solvents*

BY ARNE JENSEN AND FRED BASOLO

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The rates of reaction of bis-(cyclopentadienyl)-titanium(IV) bromide with lithium chloride and with benzyldimethyloctadecylammonium chloride to give bis-(cyclopentadienyl)-titanium(IV) chloride were investigated. The rate of reaction with the quaternary ammonium chloride in tetrahydrofuran and in benzene shows a first-order dependence on the concentration of the chloride. This suggests that the reaction takes place by a displacement (S_N2) process. Lithium chloride, under the same experimental conditions in tetrahydrofuran, reacts approximately one-twentieth as fast as does the quaternary ammonium chloride and the rate of reaction does not depend upon the concentration of lithium chloride. It is believed that in this case the rate-determining step involves a nucleophilic displacement by the solvent. The analogous bis-(cyclopentadienyl)-zirconium(IV) bromide was found to react much too fast to be studied by the spectrophotometric method used.

The mechanisms of substitution reactions of octahedral and of square metal complexes have been rather extensively investigated.[1] However, there is very little information on substitution reactions of tetrahedral metal complexes. These systems are not numerous and in general they react too rapidly to be amenable to kinetic studies by conventional techniques. Some progress has recently been made by the investigation of reactions of metal carbonyls and substituted metal carbonyls. Keeley and Johnson[2] found that the rates of carbon monoxide exchange with benzene solutions of $Ni(CO)_4$, $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$ decrease in that order. They suggest that the exchange takes place by a displacement (S_N2) mechanism. Meriwether and Fiene[3] observe that the rate of reaction of $Ni(CO)_2(PR_3)_2$ with PR_3' to yield $Ni(CO)_2(PR_3)(PR_3')$ does not depend on

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* Presented in part at the International Conference on Coördination Chemistry, London, April, 1959.

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958.

(2) D. F. Keeley and R. E. Johnson, Meeting of the American Chemical Society, Miami, Florida, April, 1957; D. F. Keeley, Doctorate Thesis, Florida State University, Tallahassee, Florida.

(3) L. S. Meriwether and M. L. Fiene, private communication.

the concentration or the nature of PR_3'. This then supports a dissociation (SN1) mechanism. It thus appears that both SN1 and SN2 mechanisms for tetrahedral metal complexes may occur, just as they are known to occur for the prototype carbon compounds.

This paper reports the results of an investigation of the reaction of bis-(cyclopentadienyl)-titanium (IV) bromide, $(C_2H_5)_2TiBr_2$, with different chlorides under various conditions to form $(C_5H_5)_2TiCl_2$. These compounds are presumed to have very nearly a tetrahedral structure in accord with the known structure of the bridged complex[4] $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$. This bridged complex was found to be a catalyst for the polymerization of ethylene.[5] A quantitative study of the rates of reaction of $(C_5H_5)_2TiBr_2$ is also of interest because there has been no previous report on the kinetics of substitution reactions of cyclopentadienyl metal halides.

Experimental

Preparation of Compounds.—Samples of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2ZrCl_2$ were generously supplied by the Union Carbide Corporation. The compounds were purified by recrystallization from boiling toluene. The corresponding bromides were prepared by a method similar to that described[6] for the synthesis of $(C_5H_5)_2TiI_2$. A solution containing 5 g. of $(C_5H_5)_2TiCl_2$ and 44 g. of anhydrous LiBr in 600 cc. of acetone was refluxed for 1 hr. The acetone was then removed and the residue was extracted with boiling toluene. When cooled in an ice-bath the toluene solution yielded 3 g. (45% yield) of the desired bromide (m.p. 310 ± 3° dec.).

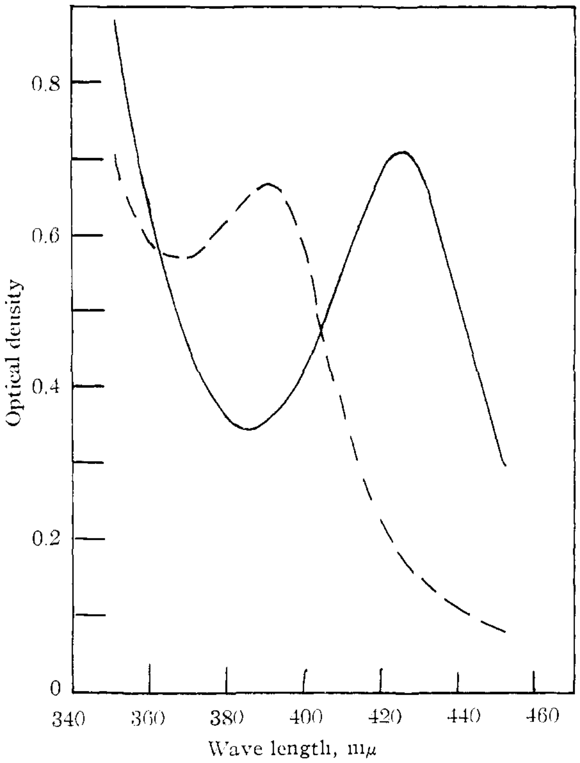

Fig. 1.—Absorption spectra of $3.0 \times 10^{-4}M$ acetone solutions of $(C_5H_5)_2TiBr_2$ ——— and $(C_5H_5)_2TiCl_2$ - - - -

Anal. Calcd. for $(C_5H_5)_2TiBr_2$: C, 35.6; H, 2.98. Found: C, 34.6; H, 3.03. The low carbon analysis is perhaps due to approximately one-half mole of water. The compound is very hygroscopic and difficult to weigh for analysis without some increase in weight.

Exactly this same procedure was used to prepare $(C_5H_5)_2ZrBr_2$ (m.p. 261 ± 1° dec.) in a 40% yield.

Anal. Calcd. for $(C_5H_5)_2ZrBr_2$: C, 31.5; H, 2.64. Found: C, 31.2; H, 2.70.

The reactants LiCl, LiBr and $(CH_3)_4NCl$ were commercially available reagent grade materials. Benzyldimethyloctadecylammonium chloride was kindly supplied by the Rohm and Haas Company. The chloride was recrystallized from acetone and this "purified" salt was found to melt at 63°.

Anal. Calcd. for $C_{27}H_{50}NCl$: C, 76.5; H, 11.9; N, 3.3. Found: C, 75.1; H, 11.8; N, 3.6.

The rates of reaction were the same whether the recrystallized or the original quaternary ammonium chloride was used. Similar difficulties have been experienced previously in the purification of large quaternary ammonium halides.[7]

Purification of Solvents.—It became apparent rather early that as little as 1% of water in tetrahydrofuran increased the rate of reaction of $(C_5H_5)_2TiBr_2$ with LiCl about ten-fold. Therefore the solvents were made as anhydrous as was conveniently possible and in the meantime they were purified.

Acetone was refluxed for 24 hr. during which time small amounts of $KMnO_4$ were added until there appeared to be no further oxidation of impurities. The solvent then was dried over anhydrous K_2CO_3 for 15 hr. and fractionally distilled, collecting the fraction that boiled at 56°. It was stored over anhydrous K_2CO_3.

Nitromethane was agitated with 1 *M* $NaHCO_3$ solution and then separated from the aqueous solution by means of a separatory funnel. After the solvent had been allowed to stand over anhydrous $CaCl_2$ for 15 hr., it was fractionally distilled and the fraction that boiled at 101° was collected. The solvent was stored over anhydrous $CaCl_2$.

Tetrahydrofuran was refluxed over NaOH pellets for 7 hr. and then for 2 hr. over metallic sodium. The solvent was then fractionally distilled and the fraction that boiled at 66° was collected and kept over sodium metal string.

The benzene was thiophene-free reagent grade, dried and kept over sodium metal string.

Rate Determinations.—The rate of reaction of $(C_5H_5)_2TiBr_2$ with LiCl was followed spectraphotometrically. It is apparent from the spectra of $(C_5H_5)_2TiBr_2$ and $(C_5H_5)_2TiCl_2$ shown in Fig. 1, that the reaction progress can be determined by measurements of the change in optical density at 425 mμ. Similarly the analogous Zr(IV) system can best be studied at 375 mμ.

Measurements of optical density (O.D.) were made using a Beckman DU spectrophotometer equipped with a thermostated cell compartment. A plot of log $(O.D.)_0 - (O.D.)_\infty / (O.D.)_t - (O.D.)_\infty$ *versus* time was linear for about 80% of the reaction. The pseudo first-order rate constant *k* was determined with a precision of better than 10%. Some studies also were made at different temperatures so that the enthalpy and entropy of activation could be calculated.

Results

The solvent effect on the rate of reaction of $(C_5H_5)TiBr_2$ with a particular chloride is shown by the data in Table I. For lithium chloride the rate of reaction in acetone is about nine times faster than it is in tetrahydrofuran. This suggests that the rate of reaction will generally be greater in the solvent of high dielectric constant. Also in this table it is seen that the reaction in tetrahydrofuran with the large quaternary ammonium chloride is about twenty-three times faster than it is with lithium chloride.

Temperature dependence studies are summarized

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[4] G. Natta, P. Corradini and I. W. Bassi, THIS JOURNAL, **80**, 755 (1958). Dipole moment measurements by L. E. Sutton (private communication) indicate that compounds of the type $(C_5H_5)_2TiX_2$ are tetrahedral.

[5] D. S. Breslow and N. R. Newburg, *ibid.*, **79**, 5072 (1957).

[6] G. Wilkinson and J. M. Birmingham, *ibid.*, **76**, 4281 (1954).

[7] C. G. Swain and M. M. Kreevoy, *ibid.*, **77**, 1122 (1955).

TABLE I

RATES OF REACTION OF $(C_5H_5)_2TiBr_2$ WITH DIFFERENT CHLORIDES IN VARIOUS SOLVENTS AT 24.9°

Solvent	Dielectric constant	Chloride	Complex × 10⁴, *M*	*k* × 10², min.⁻¹
Nitromethane	39.4	4.4×10^{-3} *M* $(CH_3)_4NCl$	4.1	20
Acetone	21.4	4.1×10^{-3} *M* LiCl	4.2	19
T.H.F.[a]	7.7	3.7×10^{-3} *M* LiCl	4.3	2.3
T.H.F.[a]	7.7	4.0×10^{-3} *M* RCl[b]	4.5	53
Benzene	2.3	4.0×10^{-3} *M* RCl[b]	2.4	100

[a] T.H.F. = tetrahydrofuran. [b] RCl = benzyldimethyloctadecylammonium chloride.

TABLE II

TEMPERATURE DEPENDENCE OF THE RATE OF REACTION OF $(C_5H_5)_2TiBr_2$ IN DIFFERENT SOLVENTS

Solvent	Temp., °C.	Chloride	$(C_5H_5)_2$-$TiBr_2$ × 10⁴, *M*	*k* × 10², min.⁻¹	E_a, kcal./mole	$\Delta S^{\ddagger}$, e.u.
Nitromethane	15.5	4.4×10^{-3} *M* $(CH_3)_4NCl$	4.4	11		
Nitromethane	24.9	4.4×10^{-3} *M* $(CH_3)_4NCl$	4.1	20	9.9 ± 1.5	−37 ± 5
Nitromethane	39.0	4.4×10^{-3} *M* $(CH_3)_4NCl$	4.1	39		
Acetone	15.5	4.1×10^{-3} *M* LiCl	2.8	11		
Acetone	24.9	4.1×10^{-3} *M* LiCl	4.2	19	9.2 ± 0.5	−39 ± 2
Acetone	39.0	4.1×10^{-3} *M* LiCl	4.1	38		
T. H. F.	15.5	3.7×10^{-3} *M* LiCl	3.4	1.3		
T. H. F.	24.9	3.7×10^{-3} *M* LiCl	4.3	2.3	8.4 ± 1.5	−46 ± 5
T. H. F.	39.0	3.7×10^{-3} *M* LiCl	3.9	3.9		

TABLE III

DEPENDENCE OF THE RATE OF REACTION OF $(C_5H_5)_2TiBr_2$ ON THE CONCENTRATION OF CHLORIDES AT 24.9°

Solvent	Chloride	$(C_5H_5)_2$-$TiBr_2$ × 10⁴, *M*	*k* × 10², min.⁻¹
Nitromethane	4.4×10^{-3} *M* $(CH_3)_4NCl$	4.1	20
Nitromethane	1.1×10^{-3} *M* $(CH_3)_4NCl$	2.1	8.4
Acetone	1.0×10^{-2} *M* LiCl	4.4	25
Acetone	4.1×10^{-3} *M* LiCl	4.2	19
T. H. F.[a]	1.0×10^{-1} *M* LiCl	4.0	5.5
T. H. F.	4.0×10^{-2} *M* LiCl	3.9	5.0
T. H. F.	2.0×10^{-2} *M* LiCl	4.0	4.6
T. H. F.	1.0×10^{-2} *M* LiCl	4.2	3.8
T. H. F.	2.0×10^{-3} *M* LiCl	3.7	2.7
T. H. F.	1.0×10^{-3} *M* LiCl	2.1	2.1
T. H. F.	2.0×10^{-2} *M* RCl[a]	3.8	>200[b]
T. H. F.	1.0×10^{-2} *M* RCl	4.3	120
T. H. F.	4.0×10^{-3} *M* RCl	4.5	53
T. H. F.	2.0×10^{-3} *M* RCl	4.7	29
T. H. F.	1.0×10^{-3} *M* RCl	1.7	16
Benzene	4.0×10^{-3} *M* RCl	2.4	100
Benzene	2.0×10^{-3} *M* RCl	2.4	58
Benzene	1.0×10^{-3} *M* RCl	2.1	26

[a] See Table I for meaning of symbols. [b] Reaction was too fast to measure by this method.

in Table II. The activation energy for these reactions is approximately 9 kcal./mole and the entropy of activation is about −40 e.u. Data in Table III show the dependence of the rate of reaction on the concentration of chloride. It is apparent from these results that the rate of reaction is zero order in lithium chloride, approximately half order in tetramethylammonium chloride and first order in the large quaternary ammonium chloride. The effect of the addition of water, methanol and phenol on the rates of reaction is shown in Table IV. It is seen that the effect decreases in the order $H_2O > CH_3OH > C_6H_5OH$. Data in this table also show that addition of lithium bromide slightly decreases the rate of reaction with lithium chloride.

Observations on the equilibrium in tetrahydrofuran solutions of about 10^{-4} *M* Ti(IV) and 10^{-2}

$$(C_5H_5)_2TiCl_2 + 2LiBr \underset{k_2}{\overset{k_1}{\rightleftarrows}} (C_5H_5)_2TiBr_2 + 2LiCl$$

M LiBr are summarized in Table V. The values of k_1 were determined from the initial portions of plots of log $[(O.D.)_\infty - (O.D.)_t]$ *vs.* time, where the optical density of $(C_5H_5)_2TiBr_2$ was used for $(O.D.)_\infty$. This can be done because the rate of reaction from right to left is negligible initially. If the experimental optical density at equilibrium is used for $(O.D.)_\infty$ then the rate constant calculated is equal to $k_1 + k_2$. This then permits an estimate of k_2. Also shown in the table are the spectrophotometrically determined ratios of the concentrations of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2TiBr_2$ at equilibrium in these solutions.

TABLE IV

EFFECT OF ADDED WATER, METHANOL, PHENOL, AND LITHIUM BROMIDE ON THE RATE OF REACTION OF $(C_5H_5)_2$-$TiBr_2$ WITH LITHIUM CHLORIDE AT 24.9°

Solvent	Solution	LiCl × 10³, *M*	$(C_5H_5)_2$-$TiBr_2$ × 10⁴, *M*	*k* × 10², min.⁻¹
Acetone	....	4.0	4.0	18
Acetone	0.56 *M* H_2O	4.2	4.3	88
Acetone	.56 *M* CH_3OH	4.2	4.7	21
Acetone	.56 *M* C_6H_5OH	4.2	4.1	12
T. H. F.	....	3.7	4.3	2.3
T. H. F.	0.56 *M* H_2O	3.9	4.1	28
T. H. F.	.56 *M* CH_3OH	3.9	4.9	5.9
T. H. F.	.56 *M* C_6H_5OH	3.9	3.8	3.0
T. H. F.	.28 *M* CH_3OH, 0.28 *M* C_6H_5OH	3.6	4.4	6.5
T. H. F.	3.2×10^{-3} *M* LiBr	4.0	4.0	2.4[a]
T. H. F.	1.0×10^{-2} *M* LiBr	4.1	3.9	3.3[a]
T. H. F.	1.0×10^{-1} *M* LiBr	3.9	4.1	2.5[a]

[a] The experimental optical density at equilibrium was used as $(O.D.)_\infty$ to determine these values. They are to be compared with values of $k \times 10^2$ min.⁻¹ of 3.4, 3.8, and 5.5, respectively, for reactions with LiCl alone of approximately the same total lithium halide concentration.

Discussion

The kinetics of the reaction

$$(C_5H_5)_2TiBr_2 + 2RCl \rightleftharpoons (C_5H_5)_2TiCl_2 + 2RBr$$

has been investigated in an attempt to determine the mechanism of substitution. The absorption spectrum of such a reaction mixture was determined at various times during the reaction. For approximately 70% of the reaction, the spectra have two isosbestic points as shown in Fig. 2. There is some decomposition on prolonged standing so that at longer times the absorbancy of the reaction mixture, particularly in the short wave length region, increases beyond what is expected for the final chloride product. However, these results indicate that during most of the reaction there is at no time any appreciable concentration of the intermediate $(C_5H_5)_2TiBrCl$. Thus it follows that this species reacts rapidly and the rate observed is then essentially its rate of formation. Alternative, but less likely, explanations of these spectra are possible. For example the results observed could be explained if the rate of reaction of the intermediate is half of that of the starting material and if the absorption spectrum of the intermediate is the exact average of that of the dibromide and the dichloride. The spectra could also be explained if the spectrum of the bromide chloride were the same as that of the dichloride.

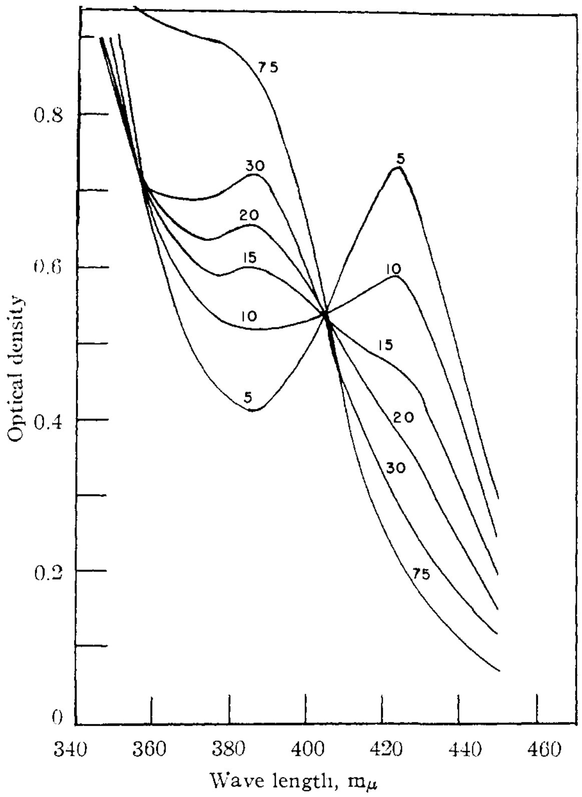

Fig. 2.—Changes in the absorption spectrum of a reaction mixture at 29° in T. H. F. containing originally $2.9 \times 10^{-4} M$ $(C_5H_5)_2TiBr_2$ and $3.6 \times 10^{-3} M$ LiCl over a period of 75 min. Numbers indicate the time in minutes that the mixture has been standing.

TABLE V

EQUILIBRIUM DATA IN TETRAHYDROFURAN ON THE SYSTEM

$$(C_5H_5)_2TiCl_2 + 2LiBr \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (C_5H_5)_2TiBr_2 + 2LiCl$$

Temp., °C.	Initial concn. $(C_5H_5)_2TiCl_2 \times 10^4$, M	LiBr $\times 10^2$, M	$k_1 \times 10^2$, min.$^{-1a}$	$k_2 \times 10^2$, min.$^{-1}$	k_1/k_2	$\frac{(C_5H_5)_2TiBr_2}{(C_5H_5)_2TiCl_2}$
15.7	1.9	1.1	0.32	0.60	0.53	0.57
15.7	2.8	0.9	.59	.76	.78	.74
15.7	4.1	1.0	.47	.79	.60	.46
					.64(av.)	.59(av.)
24.9	1.9	0.9	1.4	2.4	.56	.52
24.9	2.8	.9	1.1	2.2	.50	.64
24.9	4.1	.9	1.0	2.3	.43	.46
					.50(av.)	.54(av.)
39.0	2.2	.9	2.6	8.9	.29	.57
39.0	3.0	.9	2.5	8.1	.30	.40
39.0	3.8	.9	2.6	7.9	.33	.46
					.31(av.)	.48(av.)

[a] These values of k_1 permit estimates of $E_a = 14 \pm 3.5$ kcal./mole and $\Delta S^{\ddagger} = -29 \pm 12$ e.u.

The data in Table III show that the rate of reaction of $(C_5H_5)_2TiBr_2$ with benzyldimethyloctadecylammonium chloride in tetrahydrofuran and in benzene is first order in bromide and first order in the quaternary ammonium chloride. This chloride in these solvents of low dielectric constant is expected to be present in the form of ion-pairs.[8] At concentrations of the quaternary ammonium chloride greater than $10^{-4} M$, even triple ions begin to form.[9] Therefore at the concentrations used in these experiments quaternary ammonium chloride must be present almost entirely in the form of ion-pairs. The first-order dependence on the chloride then supports a direct displacement (SN2) by the ion-pair

$$\begin{tikzcd}
(C_5H_5)_2TiBr_2 + R^+Cl^- \arrow[r, shift left, "\text{slow}"] & (C_5H_5)_2TiBr_2{\cdot}R^+Cl^- \arrow[l, shift left] \arrow[d, shift left, "\text{fast}"] \\
 & (C_5H_5)_2TiBrCl + R^+Br^- \arrow[u, shift left] \arrow[d, shift left, "\text{fast}"] \\
 & (C_5H_5)_2TiCl_2 + R^+Br^- \arrow[u, shift left, "R^+Cl^-"]
\end{tikzcd}$$

Such a bimolecular displacement process is not unreasonable since Ti(IV) is known to have a coördination number of six. Furthermore Ti(IV) is relatively large in size and has vacant 3d orbitals, both factors would also tend to enhance any nucleophilic attack.

This same reaction with lithium chloride in tetrahydrofuran, as shown in Table III, does not depend on the concentration of lithium chloride. It is not immediately clear why lithium chloride should be a less effective reagent than is the large quaternary ammonium chloride. Such a result suggests that the chloride in lithium chloride is less nucleophilic than it is in the quaternary ammonium chloride. One explanation might be that the interaction between the lithium ion and chloride ion in its ion-pair, Li^+Cl^-, is greater than the interaction between the highly shielded nitrogen of

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(8) R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

(9) W. F. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **58**, 255 (1936).

the quaternary ammonium ion and the chloride ion of the ion-pair R^+Cl^-. It then follows that the chloride ion in Li^+Cl^- is effectively less negative or less nucleophilic than is the chloride ion in R^+Cl^-.

The zero-order dependence on lithium chloride is consistent with either a dissociation process or a displacement by the solvent followed by a rapid reaction of either the dissociated species or the solvated species with the chloride. A solvent displacement path would be analogous to the mechanism proposed for the reaction with the quaternary ammonium chloride

$$\begin{tikzcd}
(C_5H_5)_2TiBr_2 + \text{Solvent} \arrow[r, shift left, "\text{slow}"] & (C_5H_5)_2TiBr_2\cdot\text{Solvent} \arrow[l, shift left] \arrow[d, shift left, "\text{fast}"] \\
 & (C_5H_5)_2TiBrSolvent^+ + Br^- \arrow[u, shift left] \arrow[d, shift left, "\text{fast}"] \\
 & (C_5H_5)_2TiBrCl + Li^+ \arrow[u, shift left, "Li^+Cl^-"] \arrow[d, shift left, "\text{fast}"] \\
 & (C_5H_5)_2TiCl_2 + Li^+Br^- \arrow[u, shift left, "Li^+Cl^-"]
\end{tikzcd}$$

This reaction scheme also receives some support from the data shown in Table IV. The addition of water, methanol and phenol to the solvents acetone and tetrahydrofuran result in a maximum acceleration in the rate of reaction with water and the least effect with phenol. Since water is the most nucleophilic of the three added substances, it would be expected to have the greatest effect if the reaction proceeds by a displacement process. However, phenol which is the most electrophilic of the three would be expected to have the largest effect on a dissociation reaction. This would result from its greater tendency to hydrogen bond with the bromide ion in the transition state and thus promote the Ti–Br bond rupture. It is also of interest to note that a mixture of methanol and phenol is not much more effective than is estimated from the effect of each of these alone.

The solvent displacement mechanism outlined above requires that the solvated intermediate react rapidly with halide ion to form the dihalide compound. In order to see whether this happens a saturated aqueous solution of $(C_5H_5)_2TiBr_2$ was prepared. Such a water solution has been shown[6] to contain the complex ion almost entirely in the form of the hydrolysis product $(C_5H_5)_2TiH_2O(OH)^+$. A small aliquot of this solution was added to tetrahydrofuran and the spectrum of the solution was determined immediately. Within the two minutes required for this operation, the spectrum of the tetrahydrofuran solution was found to be essentially that of $(C_5H_5)TiBr_2$. Thus the solvated intermediate would seem to revert rapidly to the dihalide. Although this reaction is fast, the solvated intermediate does appear to be able to discriminate between bromide and chloride ions. Data in Table IV show that the addition of lithium bromide has only a slight retardation effect on the rate of formation of $(C_5H_5)_2TiCl_2$. For example, the reaction of 4.0×10^{-4} M $(C_5H_5)_2TiBr_2$ in tetrahydrofuran to form $(C_5H_5)_2TiCl_2$ at 25° with 1.0×10^{-1} M LiCl has a value of $k = 5.5 \times 10^{-2}$ min.$^{-1}$ whereas a value of 2.5×10^{-2} min.$^{-1}$ is obtained for the reaction with a mixture that is 3.9×10^{-3} M LiCl and 1.0×10^{-1} M LiBr. Thus even though the concentration of LiBr is twenty-five times greater than that of LiCl, the rate constant for the reaction is only decreased by a factor of two.

A few experiments were carried out with tetramethylammonium chloride in nitromethane as a solvent. In this case the rate of reaction shows approximately a half-order dependence on the concentration of the chloride. It may be that the reaction proceeds in part by direct displacement and in part by solvent displacement. There exists then a competition between the solvent and the reagent.

Data in Table I show that the rate of reaction of $(C_5H_5)_2TiBr_2$ with chlorides depends not only on the chloride but also on the solvent. In general the reaction is faster in the more polar solvent. This suggests that the transition state complex is more polar than the original compound. Such would be the case in these reactions where the Ti–Br bond separation in the transition state is expected to be greater than it is in the ground state. There would in turn be a tendency to "freeze" more solvent molecules in the transition state which is reflected in the large decrease in entropy[10] shown in Table II. The increase in rate of reaction with increasing dielectric constant of the solvent also agrees with a reaction involving ion-pairs rather than the "free" chloride ion.[11]

The reverse reaction also has been studied in tetrahydrofuran

$$(C_5H_5)_2TiCl_2 + 2Li^+Br^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} (C_5H_5)_2TiBr_2 + 2Li^+Cl^-$$

Estimates of k_1 and k_2 are given in Table V. The values of k_1 are obtained from the initial portion of the reaction where the reverse reaction is assumed to be negligible. Values of k_2 then are obtained by subtracting k_1 from k_{obs} for the equilibrium reaction. These values of k_2 are not as accurate as those determined directly and shown in Table III, but agreement with them is satisfactory. It is also of interest that the ratio of k_1/k_2 in all of these reaction mixtures is about the same as the equilibrium ratio of $[(C_5H_5)_2TiBr_2]/[(C_5H_5)_2TiCl_2)]$ in each solution. These results show that even in the presence of a relatively large concentration of lithium bromide the concentration of $(C_5H_5)_2TiCl_2$ exceeds that of $(C_5H_5)_2TiBr_2$ at equilibrium. Thus it follows that the dichloride is more stable than the dibromide. It has been pointed out[12] that in general the stability of metal halide complexes decrease with increasing atomic number of the halide ion for metal ions that do not tend to form π-bonds. Titanium(IV) in $(C_5H_5)_2TiX_2$ does not contain d orbital electrons which it could use for π-bonding with the vacant d orbitals of the halide ions. Therefore the dichloride compound

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[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 127–130.

[11] J. W. Hackett and H. C. Thomas, THIS JOURNAL, **72**, 4962 (1950).

[12] S. Ahrland, *Acta Chem. Scand.*, **10**, 723 (1956).

is expected to be more stable than the corresponding dibromide which agrees with the experimental observation.

Finally it should be mentioned that the reaction of $(C_5H_5)_2ZrBr_2$ (9.7×10^{-4} *M*) in tetrahydrofuran with LiCl (3.7×10^{-3} *M*) at 15° is complete within two minutes. Since Zr(IV) is larger than Ti(IV) the bond strength of Zr–Br probably is less than that of Ti–Br. Likewise the larger size of Zr(IV) will make it more susceptible to nucleophilic attack than is the smaller Ti(IV). Both of these factors may be responsible for the reactions of $(C_5H_5)_2ZrBr_2$ being faster than those of $(C_5H_5)_2TiBr_2$.

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EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Studies of Inorganic Coördination Complexes. XX. Cobalt(III) Ammine Complexes Containing Some Coördinated Anions[1]

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Infrared spectra of cobalt(III) ammine complexes containing NO_3^-, $CO_3^=$, $SO_3^=$, $SO_4^=$ and $S_2O_3^=$ ligands have been measured in the 2–15 μ region. The portions of the spectra arising from these coördinated anions are greatly different from those of the corresponding free anions. Assignment of the absorption bands of $[Co(NH_3)_5NO_3]Cl_2$ and $[Co(NH_3)_4CO_3]Cl$ has been accomplished by comparison of their spectra with those of (a) the deuterated analogs and (b) the organic nitrates and carbonates.

Introduction

The infrared spectra of the anions NO_3^-, $CO_3^=$, $SO_3^=$, $SO_4^=$ and $S_2O_3^=$ present as ligands in coördination complexes differ greatly from those of the free anions. These differences in spectra suggest the use of infrared spectroscopy as a method to determine if such groups are present inside or outside the coördination sphere in complex compounds. Differences in the infrared spectra of the free and coördinated anions in complex salts often result from the marked change in symmetry associated with a change in structure.[3,4] When an anion coördinates to a central metal atom of a complex, the character and configuration of the free anion are lost.

Infrared spectroscopy has been employed to determine which of several likely atoms present in a group is attached to the central metal atom in the formation of coördination complexes.[5] The infrared method should also serve to distinguish between coördination compounds in which a given group acts as a monodentate or as a bi- or polydentate ligand. Two types of complexes containing the $CO_3^=$ group are known. In one type the $CO_3^=$ group occupies one coördination position, and in the other it is said to act as a bidentate group, even though a four-membered ring results.

The present investigation was undertaken to study the change in structure of the above anions upon coördination, to determine the donor atoms in these groups and to report on the nature of the metal-to-ligand bond present in the metal coördination compounds.

Experimental

Preparation of Compounds.—Nitratopentamminecobalt(III) chloride, $[Co(NH_3)_5NO_3]Cl_2$, was prepared by the method of Jorgensen.[6]

Anal. Calcd. for $[Co(NH_3)_5NO_3]Cl_2$: NH_3, 35.25. Found: NH_3, 35.15.

Carbonatotetramminecobalt(III) chloride, $[Co(NH_3)_4CO_3]Cl$, prepared by the method of Lamb and Damon[7] was recrystallized from hot water.

Anal. Calcd. for $[Co(NH_3)_4CO_3]Cl$: Co, 26.70; N, 25.19. Found: Co, 26.89; N, 24.93.

Carbonatopentamminecobalt(III) iodide, $[Co(NH_3)_5CO_3]I$, was prepared by the method of Basolo and Murmann.[8]

Anal. Calcd. for $[Co(NH_3)_5CO_3]I$: Co, 17.81. Found: Co, 17.85.

Thiosulfatopentamminecobalt(III) chloride, $[Co(NH_3)_5S_2O_3]Cl$, was prepared by Ray's method.[9]

Anal. Calcd. for $[Co(NH_3)_5S_2O_3]Cl$: Co, 20.21. Found: Co, 20.40

Chloropentamminecobalt(III) thiosulfate, $[Co(NH_3)_5Cl]S_2O_3$, was prepared according to the method of Jorgensen.[10]

Anal. Calcd. for $[Co(NH_3)_5Cl]S_2O_3$: NH_3, 29.19. Found: NH_3, 29.19.

Sulfitopentamminecobalt(III) chloride, $[Co(NH_3)_5SO_3]Cl$ prepared by the method of Vortman and Magdeburg,[11] was recrystallized from aqueous solution.

Anal. Calcd. for $[Co(NH_3)_5SO_3]Cl$: Co, 22.70. Found: Co, 22.72.

Sulfatopentamminecobalt(III) chloride, $[Co(NH_3)_5SO_4]Cl$, was prepared by the method of Ephraim and Flugel.[12]

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